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MANUFACTURE OF AROMATIC CARBONIC ESTERS

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Abstract

Objective

To offer a method for manufacturing aromatic carbonic
esters.

Means

A method for manufacturing aromatic carbonic esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, where said reaction is carried out in the presence of (A) one or more substances selected from palladium and palladium compounds, (B) one or more substances selected from lead compounds, (C) one or more substances selected from manganese compounds, and (D) one or more substances selected from halides.

Claims

1. A method for manufacturing aromatic carbonic esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, said method for manufacturing aromatic carbonic esters being characterized in that said reaction is carried out in the presence of the following components:

(A) one or more substances selected from palladium and palladium compounds, (B) one or more substances selected from lead compounds, (C) one or more substances selected from manganese compounds, and (D) one or more substances selected from halides.

2. The method for manufacturing aromatic carbonic esters according to Claim 1, wherein the component (A) is palladium acetate, palladium bromide or palladium/carbon.

3. The method for manufacturing aromatic carbonic esters according to Claim 1, wherein the component (B) is lead oxide or a lead compound expressed by $Pb(OR)_2$ (R denotes an acyl group

with an alkyl group carbon number of 1-4, or an aryl group with a carbon number of 6-10).

4. The method for manufacturing aromatic carbonic esters according to Claim 1, wherein the component (C) is an organic acid salt of manganese or a manganese complex.

5. The method for manufacturing aromatic carbonic esters according to Claim 1, wherein the component (D) is a chloride or bromide.

6. The method for manufacturing aromatic carbonic esters according to Claim 5, wherein the component (D) is a quaternary ammonium bromide salt.

7. The method for manufacturing aromatic carbonic esters according to Claim 1, wherein the reaction temperature is in the range of 80-130°C.

8. The method for manufacturing aromatic carbonic esters according to Claim 1, wherein the component (A) is used at a mole ratio in the range of 10^{-6} to 10^{-3} with respect to the aromatic hydroxy compound.

9. The method for manufacturing aromatic carbonic esters according to Claim 1, wherein the component (B) is used at a mole ratio in the range of 10^{-5} to 10^{-2} with respect to the aromatic hydroxy compound.

10. The method for manufacturing aromatic carbonic esters according to Claim 1, wherein the component (C) is used at a mole ratio in the range of 10^{-6} to 10^{-3} with respect to the aromatic hydroxy compound.

11. The method for manufacturing aromatic carbonic esters according to Claim 1, wherein the partial pressures of carbon monoxide and oxygen are 10-100 atm and 0.2-10 atm respectively.

Detailed explanation of the invention

[0001]

Technical field of the invention

The present invention concerns a method for manufacturing aromatic carbonic esters, and more specifically, the present invention concerns a method for the manufacture of aromatic carbonic esters using a special catalyst that allows a reaction to occur between an aromatic hydroxy compound and carbon monoxide and oxygen. Aromatic carbonic esters, particularly diphenyl carbonic, are useful as raw materials in the production of polycarbonic and other substances.

[0002]

Prior art

In the past, methods wherein an aromatic hydroxy compound and phosgene are allowed to react have been used for manufacturing aromatic carbonic esters. However, these methods are undesirable due to the high toxicity of phosgene. Thus, methods have been offered that do not use phosgene whereby aromatic carbonic esters are manufactured by a reaction between an aromatic hydroxy compound and carbon monoxide and oxygen.

With regard to catalysts that are used in such methods, a method is described in Japanese Kokoku Patent No. Sho 56[1981]-38144 wherein a palladium compound, a compound containing a metal from group IIIA, IVA, VA, VIA, IB, IIB, VIB or VIIB of the periodic table and a base are used; a method is described in Japanese Kokoku Patent No. Sho 56[1981]-38145 wherein a palladium compound, manganese complex, cobalt complex, base and desiccant are used; a method is described in Japanese Kokai Patent Application No. Hei 1[1989]-165551 wherein a palladium compound, iodine compound and zeolites are used; a method is described in Japanese Kokai Patent Application No. Hei 2[1990]-104564 wherein a palladium compound, divalent or trivalent manganese compound, tetraalkylammonium halide and quinones are used; a method is described in Japanese Kokai Patent Application No. Hei 2[1990]-142754 wherein a palladium compound, cobalt compound, tetraalkylammonium halide and quinones are used; a method is described in Japanese Kokai Patent Application No. Hei 5[1993]-25095, wherein a palladium or palladium compound, cobalt compound, halide and basic compound are used; a method is described in Japanese Kokai Patent Application No. Hei 5[1993]-39247 wherein a palladium compound, copper compound, quinones and onium halide are used; a method is described in Japanese Kokai Patent Application No. Hei 5[1993]-58961 wherein palladium or one or more palladium compounds, a cobalt compound and alkali metal halide are used; a method is described in Japanese Kokai Patent Application No. Hei 5[1993]-97775 wherein (a) a palladium compound, (b) a quaternary ammonium salt, (c) a metal auxiliary catalyst selected from among cobalt, iron,

cerium, manganese, molybdenum, samarium, vanadium, chromium and copper, and (d) an organic auxiliary catalyst selected from an aromatic ketone, aliphatic ketone and aromatic polycyclic hydrocarbon are used; a method is described in Japanese Kokai Patent Application No. Hei 6[1994]-9505, wherein a palladium compound, cerium compound and quaternary ammonium salt are used; a method is described in Japanese Kokai Patent Application No. Hei 6[1994]-41020 wherein (a) a palladium compound, (b) a metal auxiliary catalyst selected from manganese, cobalt and copper and (c) a nitrile compound are used; a method is described in Japanese Kokai Patent Application No. Hei 6[1994]-172268 wherein a palladium compound, penta-coordinated cobalt complex and quaternary onium salt are used; a method is described in Japanese Kokai Patent Application No. Hei 6[1994]-172269 wherein (a) a palladium compound, (b) an inorganic auxiliary catalyst selected from cobalt, manganese and copper, (c) a quaternary onium salt and (d) terpyridine or other organic co-catalyst are used; and a method is described in Japanese Kokai Patent Application No. Hei 6[1994]-211750 wherein a palladium compound, a monovalent or divalent copper compound and an ammonium halide compound are used. In addition, with regard to methods for managing the catalytic reaction, a method is described in Japanese Kokai Patent Application No. Hei 7[1995]-188116 wherein a precious metal catalyst is activated in a carbon monoxide atmosphere; and a method is described in Japanese Kokai Patent Application No. Hei 7[1995]-247243 wherein a reaction is carried out while removing the water that is a by-product of the reaction.

[0004]

The inventors of the present invention carried out experiments such as addition testing using conventional catalysts with phenol as a substrate, and determined that, with all of the catalysts, aromatic carbonic ester structural isomers, such as phenyl salicylate and other o-hydroxy aromatic carbonic aryl esters, are produced as by-products. In general, said isomers are compounds that are extremely difficult to separate from the aromatic carbonic esters by means of distillation or other methods. A method wherein a palladium compound, lead compound and quaternary onium halide salt are used as in a key catalyst has been offered in the specification of European Laid-Open Patent Application No. 0663388 to reduce the amount of by-product that is difficult to separate. The objective of the present invention is thus to offer a method for the efficient manufacture of aromatic carbonic esters while achieving higher rates of production of the desired aromatic carbonic esters and maintaining the effect of the catalyst.

[0005]

Means to solve the problems

The inventors of the present invention as a result of painstaking investigations concerning a solution to the problems described above, arrived at the present invention upon discovering that by-production of o-hydroxy aromatic carboxylic acid aryl esters can be controlled, and aromatic carbonic esters can be obtained with good efficiency, by allowing a reaction to

occur between an aromatic hydroxy compound and oxygen and carbon monoxide in the presence of a special catalyst. Specifically, the present invention is a method for manufacturing aromatic carbonic esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, said method for manufacturing aromatic carbonic esters being characterized in said reaction is carried out in the presence of the following components: (A) one or more substances selected from palladium and palladium compounds, (B) one or more substances selected from lead compounds, (C) one or more substances selected from manganese compounds, and (D) one or more substances selected from halides. The present invention is described in detail below.

[0006]

Mode of implementation of the invention

1. Reaction raw materials

1) Aromatic hydroxy compound

The aromatic hydroxy compound that is used in the present invention can be any substance, provided that it is an aromatic mono- or polyhydroxy compound. Examples include phenol; cresol, xyleneol, trimethylphenol, tetramethylphenol, ethylphenol, propylphenol, methoxyphenol, ethoxyphenol, chlorophenol, dichlorophenol, bromophenol, dibromophenol and other substituted phenols and isomers thereof; naphthol, methylnaphthol, ethylnaphthol, chloronaphthol, bromonaphthol and other substituted naphthols and isomers thereof;

2,2'-bis(4-hydroxyphenyl)propane and various other bisphenols; various biphenols; various hetero-aromatic hydroxy compounds and isomers thereof, and compounds formed by the substitution of alkyl groups or halogen atoms thereupon. Phenol is particularly desirable among these substances.

[0007]

(2) Carbon monoxide

The carbon monoxide in a gaseous state that is used in the present invention is produced by starting with a high-purity substance and diluting it with another gas that does not have a detrimental influence on the reaction, such as air, argon, carbon dioxide or hydrogen.

[0008]

(3) Oxygen

The oxygen in a gaseous state that is used in the present invention is produced by starting with a high-purity substance and diluting it with another gas that does not have a detrimental influence on the reaction, such as air, nitrogen, argon, carbon dioxide or hydrogen.

2. Catalyst

The catalyst that is used in the reaction of the present invention is a substance that contains a system that is a combination of one or more of each of the substances listed for each of the components (A), (B), (C) and (D) below.

(A) Palladium and palladium compounds

The palladium and palladium compounds that are used in the present invention are palladium black, palladium/carbon, palladium/alumina, palladium/silica or other carried palladium; palladium chloride, palladium bromide, palladium iodide, palladium sulfate, palladium nitrate or other inorganic palladium salts; and palladium acetate, palladium oxalate or other organic palladium acid salts. In addition, substances that can also be used include palladium (II) acetylacetonate, palladium complexes produced by the coordination of carbon monoxide, nitriles, amines, phosphines or olefins on palladium, examples of which include $\text{PdCl}_2(\text{PhCN})_2$, $\text{PdCl}_2(\text{PPh}_3)_2$, $\text{Pd}(\text{CO})(\text{PPh}_3)_3$, $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$, $\text{Pd}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$, $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$, $\text{Pd}(\text{DBA})_2$ and $\text{Pd}_2(\text{DBA})_3 \cdot \text{CHCl}_3$ (where DBA denotes dibenzylidene acetone); or mixtures of coordinated compounds formed between these complexes in the reaction system and palladium or palladium compounds. Of these substances, palladium acetate, palladium bromide and palladium/carbon are preferred. The amount of palladium component that is used in the present invention is preferably selected from a mole ratio in the range of 10^{-7} to 10^{-2} with respect to the

aromatic hydroxy compound, with a range of 10^{-6} to 10^{-3} being particularly desirable.

[0010]

(B) Lead compound

The lead compound that is used in the present invention is preferably a compound that is soluble in the liquid phase under the reaction conditions, examples of which include PbO , Pb_3O_4 , PbO_2 and other lead oxides; lead (II) acetate, lead tetraacetate, lead (II) oxalate, lead (II) propionate and other organic acid salts of lead; lead (II) sulfate, lead (II) nitrate and other inorganic salts of lead; $Pb(OMe)_2$, $Pb(OPh)_2$ and other alkoxy leads and aryloxy leads; and phthalocyanine lead and other lead complexes. Of these substances, lead compounds expressed by $Pb(OR)_2$ (where R denotes an acyl group with an alkyl group carbon number of 1-4 or an aryl group with a carbon number of 6-10) are preferred. There are no particular restrictions on the amount of lead compound that is used in the present invention, but it is preferable to use a mole ratio in the range of 10^{-5} to 10^{-1} with respect to the aromatic hydroxy compound, with a range of 10^{-5} to 10^{-2} being preferred.

[0011]

(C) Manganese compound

The manganese compound that is used in the present invention is a divalent, trivalent or tetravalent manganese compound.

Specific examples include manganese (II) oxide, manganese dioxide and other manganese oxides, manganese (II) chloride, manganese (II) bromide, manganese (II) sulfate, manganese (II) nitrate and other inorganic manganese salts; manganese (II) acetate, manganese (III) acetate, manganese (II) oxalate, manganese (II) benzoate and other organic manganese salts; and manganese (II) acetylacetonate, manganese (III) acetylacetonate, phthalocyanine manganese and manganese (II)

N,N'-bis(salicylidene)ethylenediamine. Of these compounds, complexes of manganese and organic acid salts of manganese are preferred. There are no specific restrictions on the amount of manganese compound that is used in the reaction, but a mole ratio in the range of 10^{-7} to 10^{-2} with respect to the aromatic hydroxy compound is preferred, with a range of 10^{-6} to 10^{-3} being particularly desirable.

[0012]

(D) Halide

The halide that is used in the present invention is preferably a substance that is soluble in the liquid phase under the reaction conditions, and chlorides and bromides are particularly desirable. Specific examples include cesium chloride, sodium bromide, potassium bromide, rubidium bromide, cesium bromide, barium bromide and other inorganic halides; tetra-n-butylammonium bromide, tetramethylammonium bromide and other quaternary ammonium halide salts; tetraphenylphosphonium bromide, methyltriphenylphosphonium bromide, and other quaternary phosphonium halide salts. Of these substances, quaternary

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ammonium bromide salts are preferred. There are no specific restrictions on the amount of halide that is used in the present invention, but a mole ratio in the range of 10^{-5} to 1 with respect to the aromatic hydroxy compound is desirable, with a range of 10^{-4} to 10^{-1} being preferred.

[0013]

3. Reaction conditions

The reaction is performed by introducing the aforementioned aromatic hydroxy compound and the catalyst comprising a combination of one or more of each of the aforementioned components (A), (B), (C) and (D), and then carrying out the reaction while heating after pressurizing the system with the aforementioned carbon monoxide and oxygen. The absolute pressure during the reaction is in the range of 1-500 atm, with 1-150 atm being preferred. Based on considerations pertaining to stability, the mixing ratio of the carbon monoxide and oxygen is preferably a value that is distant from the combustion range. The partial pressures of the carbon monoxide and oxygen are 10-100 atm and 0.2-10 atm respectively, and the reaction temperature is in the range of 20-300°C, with 80-130°C being preferred. Although the reaction time will differ depending on the reaction conditions, the reaction time is ordinarily a few minutes to a few hours. During the reaction, hydroquinone and other such aromatic diols, quinones that are oxidation products thereof, and amines or other organic additives, which are used in conventional catalyst systems, can be added to the reaction system. In addition, examples of solvents that can be used include inert solvents such

as hexane, heptane, cyclohexane, benzene, toluene, xylene, methylene chloride, chloroform, chlorobenzene, ethyl ether, phenyl ether, tetrahydrofuran, dioxane and acetonitrile. There are cases where the raw material aromatic hydroxy compound serves as the reaction solvent and it is not particularly necessary to use another solvent in such cases.

[0014]

Application examples

The present invention is described in detail below by providing application examples and comparative examples. The present invention is not restricted to these application examples, provided that the gist of the invention is not superseded.

Application Example 1

3.0 g (32 mmol) of phenol, 2.6 mg (1.2 μ mol Pd) of 5% palladium/carbon (N.E. Chemcat), 1.3 mg (6.0 μ mol) of lead (II) oxide, 0.48 mg (2.0 μ mol) of manganese (II) acetate tetrahydrate and 18 mg (0.12 mmol) of tetramethylammonium bromide were introduced into a Hastelloy autoclave with an inner volume of 40 mL. After replacing the interior of the system with carbon monoxide, carbon monoxide was introduced at 60 atm, dry air was introduced at 30 atm, and the reaction was mixed by stirring for 1 h at 100°C using a stirring bar. After completion of the reaction, the reaction solution was subjected to quantitative analysis by gas chromatography. The results were a yield of 5.9%

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(0.95 mmol) of diphenyl carbonic with respect to phenol. The phenyl salicylate by-product was produced at 0.73% with respect to the diphenyl carbonic.

[0015]

Application Examples 2-5

Experimentation was carried out in the same manner as in Application Example 1, with the exception that 2.0 μ mol of each of various manganese compounds was used instead of the manganese (II) acetate tetrahydrate. The yield of resulting diphenyl carbonic with respect to phenol, and the by-product ratio of phenyl salicylate with respect to diphenyl carbonic is shown in Table I.

[0016]

Table I

//insert//

Key: 1 Application example
2 Manganese compound
3 Diphenyl carbonic (%)
4 Phenyl salicylate (%)
5 Manganese (II) acetylacetonate dihydrate
6 Manganese (III) acetylacetonate
7 Manganese (II) phthalocyanine
8 Manganese (II) N,N'-bis(salicylidene)ethylenediamine

[0017]

Comparative Example 1

The same reaction as in Application Example 1 was carried out, with the exception that manganese (II) acetate tetrahydrate was not used. The results were a diphenyl carbonic yield of 2.0% (0.33 mmol) with respect to phenol.

[0018]

Comparative Example 2

The same reaction as in Application Example 1 was carried out, with the exception that lead (II) oxide was not used. The results were a diphenyl carbonic yield of 1.2% (0.19 mmol) with respect to phenol. In addition, phenyl salicylate was produced as by-product at 3.6% with respect to the diphenyl carbonic.

[0019]

Application Example 6

The same reaction as in Application Example 1 was carried out, with the exception that 2.3 mg (6.0 μmol) of lead (II) acetate trihydrate was used instead of lead (II) oxide. The results were a diphenyl carbonic yield of 5.6% (0.89 mmol) with respect to phenol. In addition, phenyl salicylate was produced as by-product at 0.75% with respect to diphenyl carbonic.

[0020]

Application Example 7

12.6 g (134 mmol) of phenol, 0.45 mg (2.0 μmol) of palladium acetate, 6.6 mg (30 μmol) of lead (II) oxide, 0.58 mg (2.4 μmol) of manganese (II) acetate tetrahydrate and 39 mg (0.25 mmol) of tetramethylammonium bromide were introduced into a Hastelloy autoclave with an inner volume of 50 mL. After replacing the interior of the system with carbon monoxide, carbon monoxide was introduced at 40 atm, and dry air was introduced at 20 atm. The reactants were mixed by stirring for 2 h at 100°C using a stir bar. After completion of the reaction, the reaction solution was subjected to quantitative analysis by means of gas chromatography. The results were a diphenyl carbonic yield of 3.0% (2.0 mmol) with respect to the phenol. In addition, phenyl salicylate was produced as by-product at 0.59% with respect to the diphenyl carbonic.

[0021]

Application Example 8

A reaction was allowed to occur in the same manner as in Application Example 7, with the exception that 0.56 mg (2.1 μ mol) of palladium bromide was used instead of palladium acetate. The results were a diphenyl carbonic yield of 2.7% (1.8 mmol) with respect to the phenol. In addition, phenyl salicylate was produced as by-product at 0.60% with respect to the diphenyl carbonic.

[0022]

Application Example 9

12.2 g (130 mmol) of phenol, 10 mg (4.8 μ mol Pd) of 5% palladium/carbonic (N.E. Chemcat), 5.4 mg (24 μ mol) of lead (II) oxide, 2.0 mg (8.0 μ mol) of manganese (II) acetate tetrahydrate, and 151 mg (0.98 mmol) of tetramethylammonium bromide were introduced into a Hastelloy autoclave with an inner volume of 50 mL. After replacing the interior of the system with carbon monoxide, carbon monoxide was introduced at 40 atm, and 4% oxygen/nitrogen was introduced at 25 atm. The reactants were mixed by stirring for 2 h at 100°C using a stir bar. After completion of the reaction, the reaction solution was subjected to quantitative analysis by gas chromatography. The results were a diphenyl carbonic yield of 3.3% (2.1 mmol) with respect to the phenol. In addition, phenyl salicylate was produced as by-product at 1.4% with respect to the diphenyl carbonic.

[0023]

Effect of the invention

As is clear from the results presented above, aromatic carbonic ester can be produced efficiently by means of the present invention while controlling production of by-product that is difficult to separate by distillation. The present invention thus offers a method for manufacturing aromatic carbonic esters with high industrial value.

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